63-4-5

UNCLASSIFIED

UNIFORM WORK FUNCTION CATHODE STUDIES FOR THERMIONIC CONVERTERS

FOURTH QUARTERLY REPORT

JULY 1963

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

BPS 2 - 6799 - 760E - 415604

(PREPARED UNDER CONTRACT NO. AF 33(657)-8726 BY ATOMICS INTERNATIONAL, A DIVISION OF NORTH AMERICAN AVIATION, INC., CANOGA PARK, CALIFORNIA; M. N. HUBERMAN, AUTHOR.)

UNCLASSIFIED

NOTICES

UNIFORM WORK FUNCTION CATHODE STUDIES FOR THERMIONIC CONVERTERS

FOURTH QUARTERLY REPORT

JULY 1963

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

BPS 2 – 6799 760E – 415604

(PREPARED UNDER CONTRACT NO. AF 33(657)-8726 BY ATOMICS INTERNATIONAL, A DIVISION OF NORTH AMERICAN AVIATION, INC., CANOGA PARK, CALIFORNIA; M. N. HUBERMAN, AUTHOR.)

FOREWORD

The work reported here was performed by Atomics International, A Division of North American Aviation, Inc., under the direction of the Electronic Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. Lawrence E. Porter is project engineer for the Laboratory.

This report describes the progress made during the fourth quarter (12 April 1963 to 12 June 1963) in addition to reviewing the overall progress of a program to study methods of improving the uniformity of work function of thermionic converter cathodes under Contract No. AF33(657)-8726. The study program is under the technical direction of M. N. Huberman of the Thermionics and Thermoelectrics Department of Atomics International. Messrs. E. V. Clark and R. A. Mohr were major contributors to the work reported herein.

CONTENTS

FIGURES

ABSTRACT

Work during the fourth quarter of a program to produce uniform work function cathodes is described. A thermionic emission electron microscope for observing work function uniformity has been constructed. Arc cast, single crystal, and vapor deposited molybdenum cathodes have been examined with the microscope. Active spots due to electropolishing were observed on the (110) face of the single crystal. A vapor deposited cathode was found to have areas of uniform work function. A brief summary is made of the overall course of the first year of the program and its most significant achievements.

I. INTRODUCTION

The general purpose of this study program is to improve the efficiency of thermionic converters which have nonplanar geometries. Specifically, the investigation concerns the production of nonplanar cathodes having more uniform work functions and surface characteristics than are obtained with standard cathode fabrication techniques. This report describes progress of the study from April 12, 1963 to June 30, 1963 in addition to a brief summary of the year's progress.

Previous reports for this program have described the use of chemical vapor deposition techniques to obtain preferred crystallographic orientations in vapor deposited molybdenum. Standard x-ray techniques were used to determine the orientations and it was concluded that (111) and (100) fiber orientations could be produced by both chemical reduction of molybdenum hexafluoride and pyrolysis of molybdenum pentachloride, but stricter control of deposition conditions would be needed before reliable reproducibility could be obtained.

The past quarter's work consisted mainly of the design and construction of a thermionic emission microscope for directly examining the uniformity of work function of vapor deposited surfaces. After successful completion of the microscope, several samples, to be described, were examined with the microscope.

II. SUMMARY OF PROGRESS

The year's most significant achievements are listed below.

An investigation has been made of the effects of different processes and different process parameters in the chemical vapor deposition of molybdenum. The investigation included both metallographic and x-ray analysis of all samples produced.

It has been shown that pyrolysis of molybdenum pentachloride and chemical reduction of molybdenum hexafluoride are both capable of producing either (111) or (100) orientations in vapor deposited molybdenums. Reproducibility and uniformity on a large scale, however, have not been achieved.

It has been shown that mechanical polishing followed by heat treatment preserves the preferred orientation at the surface. Heat treatment removes deformations in the metal structure and returns the surface layer to its original orientation.

Testing of a cylindrical thermionic diode with an arc cast cathode has shown this type of diode to be reproducible to within 5% at an emitter temperature of 1800°C.

A thermionic emission electron microscope has been built and demonstrated to be an adequate instrument for observing work function variations on cathode surfaces.

It has been shown that a vapor deposited molybdenum cathode has areas in which there is no observable differences in emission among the various grains.

The uniform emission occurred over low work function areas which correlated well with the (111) orientation sample. By extending the area of uniformity it will be possible to fabricate molybdenum cathodes having much higher vacuum thermionic emission current densities than attainable with normal randomly oriented molybdenum.

III. EMISSION MICROSCOPE

Figure 1 is a photograph of the completed microscope. Figures 2 and 3 are closeups of the microscope interior. The basis of the microscope is the three electrode cathode immersion lens as first studied by Johannson[1] (Figure 4). The lens dimensions are approximately the same as used by Johannson.[1] G_1 and G_2 were made from 5-mil molybdenum sheet while A was machined from type 304 stainless steel. Brass support posts and a lavite insulating base plate are used to maintain the desired electrode spacing and alignment. A tapered cylinder fabricated from 3-mil stainless steel sheet is joined to the after part of the anode to provide a field free drift region for the electrons emerging from the lens. A flexible bellows mounted three way movable cathode support, similar to Jensen's design,[2] allows adjustment of the cathode to grid spacing for focusing and lateral movement for scanning the cathode surface. The cathode is heated from the rear by electron bombardment. The bombardment filament and sample are mounted as an integral unit to facilitate cathode positioning. Typical bombardment requirements for 1800°C operating temperature are 790 volts and 40 milliamps.

An unregulated 5-kv 1-amp power supply in conjunction with resistance voltage dividers is used for all electrode voltages. Since the important parameters in determining the optical constants for a given lens configuration are the electrode voltage ratios V_1/V_A and V_2/V_A rather than the absolute voltage magnitudes, the use of voltage dividers with one supply allows these ratios to be constant independent of supply fluctuations. The voltage divider network is shown in Figure 5.

S_1 provides a coarse adjustment of V_{G2}/V_A. The potentiometers R_1 and R_{11} are coupled in tandem to the fine adjustment S_2 so that a continuous adjustment can be made to any desired value between successive settings of S_1.

Since G_1 normally runs at zero or negative with respect to the cathode, the method used is to ground G_1 and use a separate voltage divider to bias C positive with respect to G_1. The bombardment supply is run with both terminals floating, so that changing the cathode potential has no effect on the heating power.

The cathode samples are normally 3/16-inch diameter by 1/16-inch thick disks. A pyrex window at the side of the microscope allows direct viewing of

7-22-63

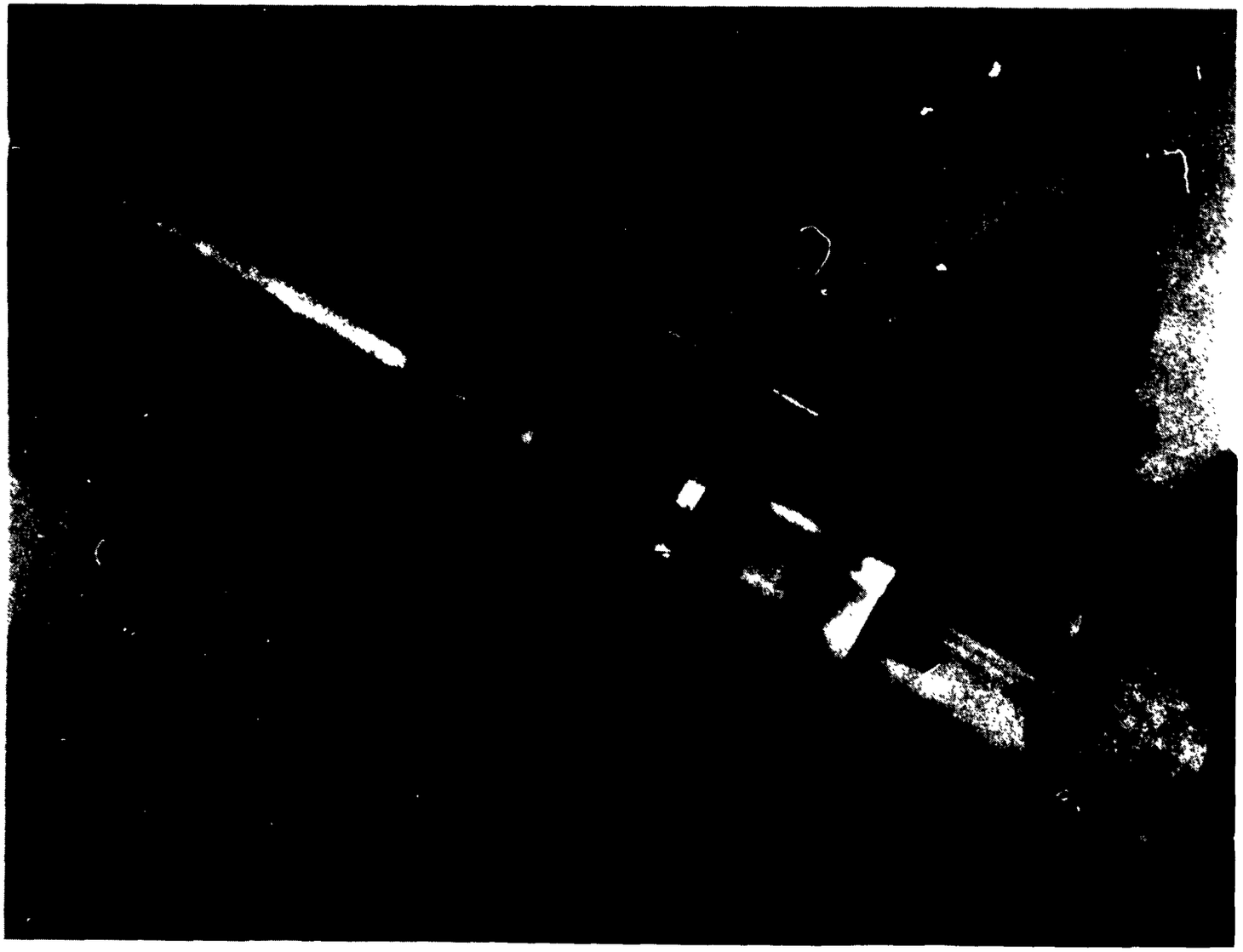
2449-1801

Figure 1. Thermionic Emission Electron Microscope

5-15-63

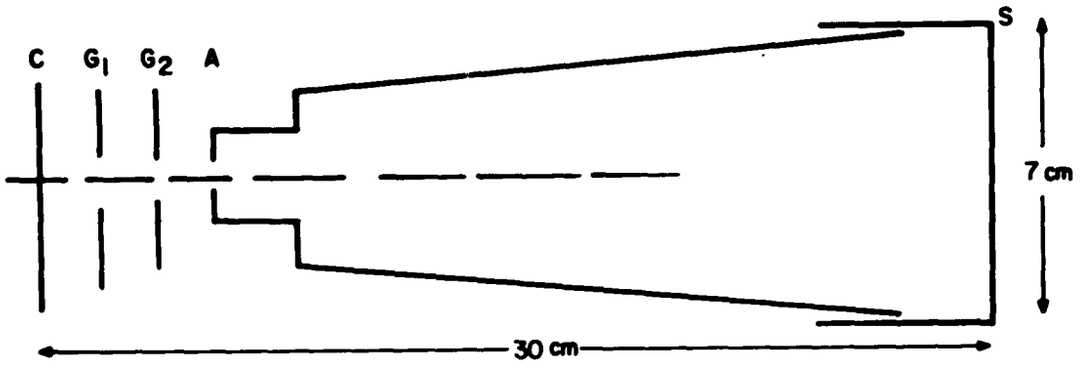
2449-5502

Figure 2. Microscope Interior



5-15-63 2449-5501

Figure 3. Microscope Lens and Cathode Closeup



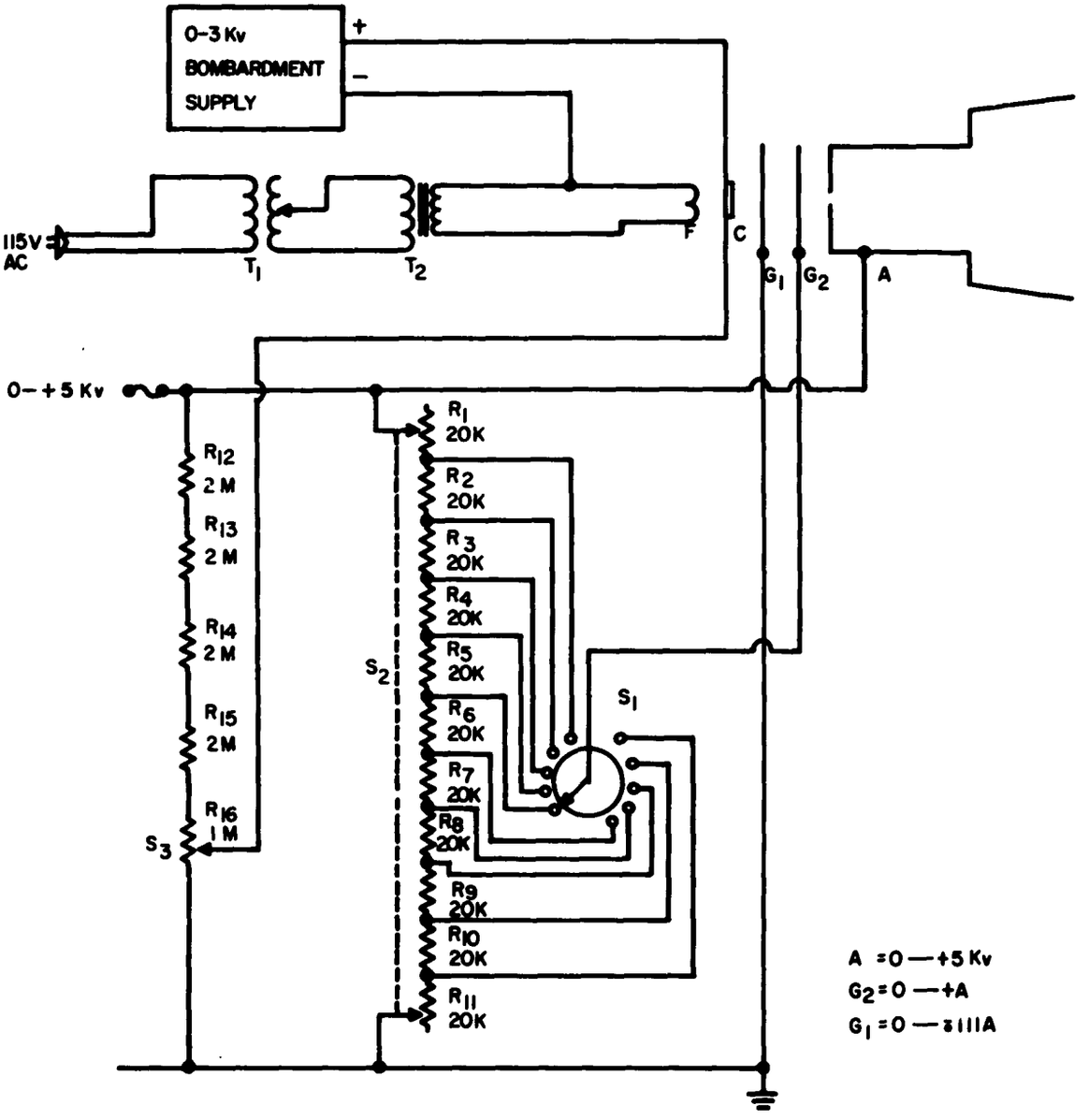
G_1 = 1st Grid (aperture diameter = 1.1 mm)
G_2 = 2nd Grid (aperture diameter = 1.0 mm)
A = Anode (aperture diameter = 1.0 mm)
S = Screen
$G_1 - G_2$ = 0.48 mm
G_2 - A = 0.72 mm

Figure 4. Cathode Immersion Lens (Not Drawn to Scale)

the cathode while positioning it and also for making optical pyrometer temperature measurements. Pyrometer readings can be taken from either a black body hole in the side of the sample or directly from the sample side (correcting for the emissivity of molybdenum).

A 3-inch ID 10-inch by 10-inch pyrex cross is used for the projection tube. A brass housing containing the cathode viewing window, an ionization gauge, and two high voltage lead-throughs is attached to one end of the tube. The entire cathode and lens assembly is mounted on a base plate which serves as the end seal for the brass housing when fully assembled. Standard O-ring seals are employed.

The opposite end of the pyrex cross contains the fluorescent screen and is sealed with a pyrex end plate. The interior of the screen end is coated with aquadag to form a continuous conducting envelope with the steel cone. Satisfactory fluorescent screens are obtained by removing the screen end of surplus 3FP7A cathode ray tubes. Future plans, however, are to switch to a shorter persistence screen to facilitate focusing.



G_1 = 1st Grid

G_2 = 2nd Grid

A = Anode

C = Cathode

F = Electron Bombardment Filament

Figure 5. Microscope Wiring Diagram

Of the two remaining ends of the cross, one is bolted directly to a two-inch vacuum system while the other is blanked off. Normal operating vacuum for the microscope is 1 to 3 x 10^{-5} torr. It was necessary to physically remove the mechanical roughing pump from the vacuum system cart and use a long rubber hose coupling in order to eliminate vibration.

The microscope is normally operated at 3 kv, occasionally as high as 4.5 kv. The magnification at the screen is 112. Following Heidenreich,[3] the theoretical limit of resolution of the microscope is of the order kT/E, where T is the cathode temperature (°K), kT is measured in volts, and E is the field strength at the cathode. For T = 2100°K and E approximately 10^4 volts/cm, the theoretical limit of resolution is thus of the order of 2000Å. It is believed the actual resolution of the microscope is of the order of 20,000Å.

IV. EMISSION STUDIES

Single crystal, vapor deposited, and standard stock molybdenum samples were examined in the emission microscope during the last month of the quarter. This section describes the samples used and observed results.

The samples were 3/16-inch diameter by 1/16-inch thick disks. With the exception of the single crystal, to be described, no chemicals or etchants were used. After preliminary polishing with 400 and 600 silicon carbide papers, the surfaces were finished down successively with 14, 6, 1, and 1/4 micron diamond paste. Final scratches were removed with Linde B alumina abrasive. Buehler 40-7158 AB Metcloth was used for the diamond paste and Buehler 40-7208 AB Microcloth for the final Linde B polishing. Since the vapor depositions were of the order of 10 mils thick, extreme care was exercised not to remove any more material than was absolutely necessary to obtain an even finish. Usually 2 to 3 mils were removed during polishing. Since the operating temperatures in the emission microscope are high enough to recrystallize the disturbed surface layer, no chemical etching was needed.

Figures 6 and 7 are emission photographs taken with commercial arc cast molybdenum. It is apparent that the microscope is more than adequate to resolve the various grains and that emission differences from one grain to another produce an easily discernible contrast. In fact, four different work functions are apparent in Figure 7.

It is also possible to follow grain growth and its effect on emission. Figures 8a and 8b respectively show the same sample before and after a surface change due to grain growth. The photographs were taken approximately one minute apart, with the sample at 1750°C. Remnants of the old grain boundaries and imperfections in 8a are still visible in 8b.

An electropolished (110) single crystal face was looked at. The polishing electrolyte was a solution of 5% sulphuric acid, 1-1/4% hydrofluoric acid, 93-3/4% methanol. As expected, no grain structure was observed. Unlike any of the other samples, the single crystal was covered with small active patches of the order of micron dimensions (Figure 9). Such active patches have been observed before with chemically polished cathodes[4] and may be due to inclusions

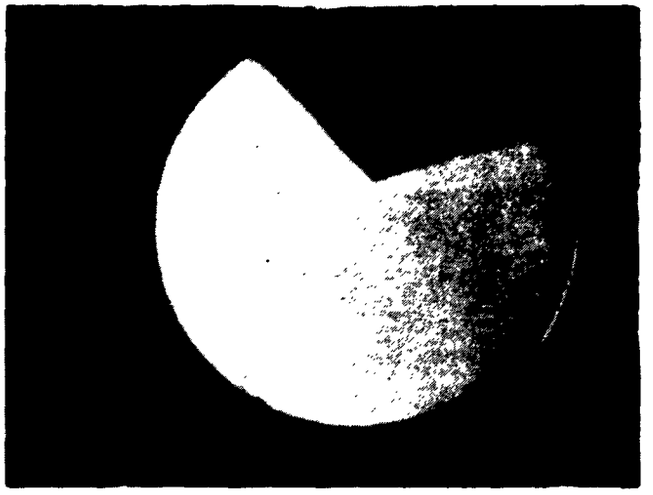


Figure 6. Arc Cast Molybdenum
Emission Micrograph (100 x)

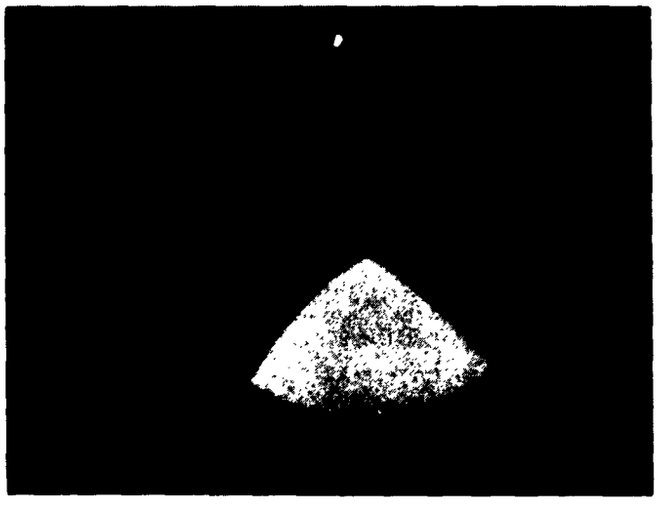


Figure 7. Arc Cast Molybdenum
Emission Micrograph (100 x)

8a. Prior to Grain Transformation

8b. Same Area One Minute Later

Figure 8. Emission Micrograph of Grain Growth in Arc Cast Molybdenum (125X)

or etch pits. The surface of the cathode used to obtain Figure 9 had been damaged in handling prior to insertion in the microscope, however, and the experiment should be repeated before it is 100% certain that the patches are indeed due to the polishing. Several vapor deposited samples were examined. The first few samples did not exhibit uniformity of work function (Figure 10) although the characteristically smaller grain diameter of the vapor depositions was observed. One sample produced by fluoride reduction did show patches of uniform work function (Figure 11), in which the boundaries between adjacent identically emitting grains was just barely resolved.

It was found that while the microscope was more than adequate to resolve individual grains, its limit of resolution was of the order of the width of the grain boundaries. Also, the effects of lens aberrations began to be significant. Thus, in Figure 11 only some of the grain boundaries are just barely evident, while aberrations obscure them over the rest of the microscope screen. In the laboratory, the positions of the other grain boundaries can be observed by positioning the cathode until they are in focus. Of course, this defocuses the ones that are already visible.

X-ray analysis showed the sample to have a (111) fiber orientation. This is in good agreement with the fact that the uniform work function patches were the brightest, hence the lowest work function, areas on the sample.

It can be concluded that vapor deposition does produce clusters of grains having the same work function. However, further experimentation with vapor deposition is needed to attain reproducibility and uniformity over an entire sample.

The previous quarterly report discussed the possibility of using an electron mirror microscope to examine patch effects. Since it is now apparent that the emission microscope produces a much higher contrast between work functions, it has been decided to confine the studies to the emission microscope.

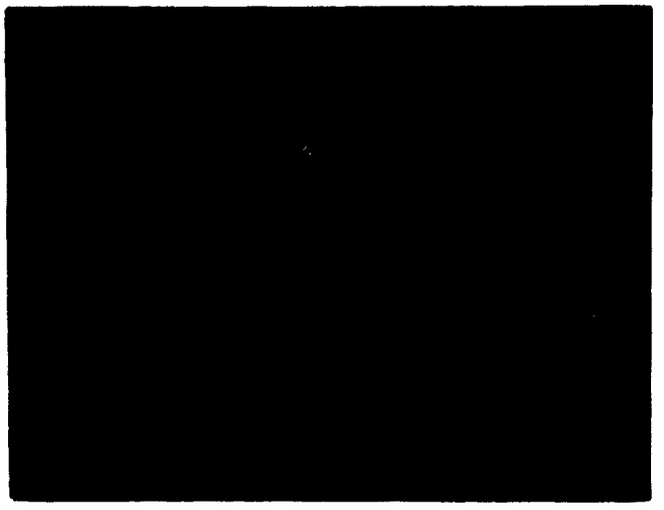


Figure 9. Electropolished Single Crystal Emission Micrograph (100X)

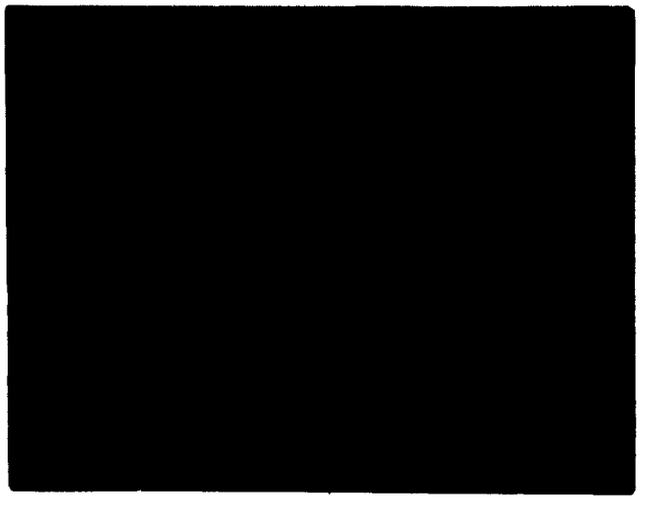


Figure 10. Emission Micrograph of Vapor Deposted Nonuniform Cathode (100X)

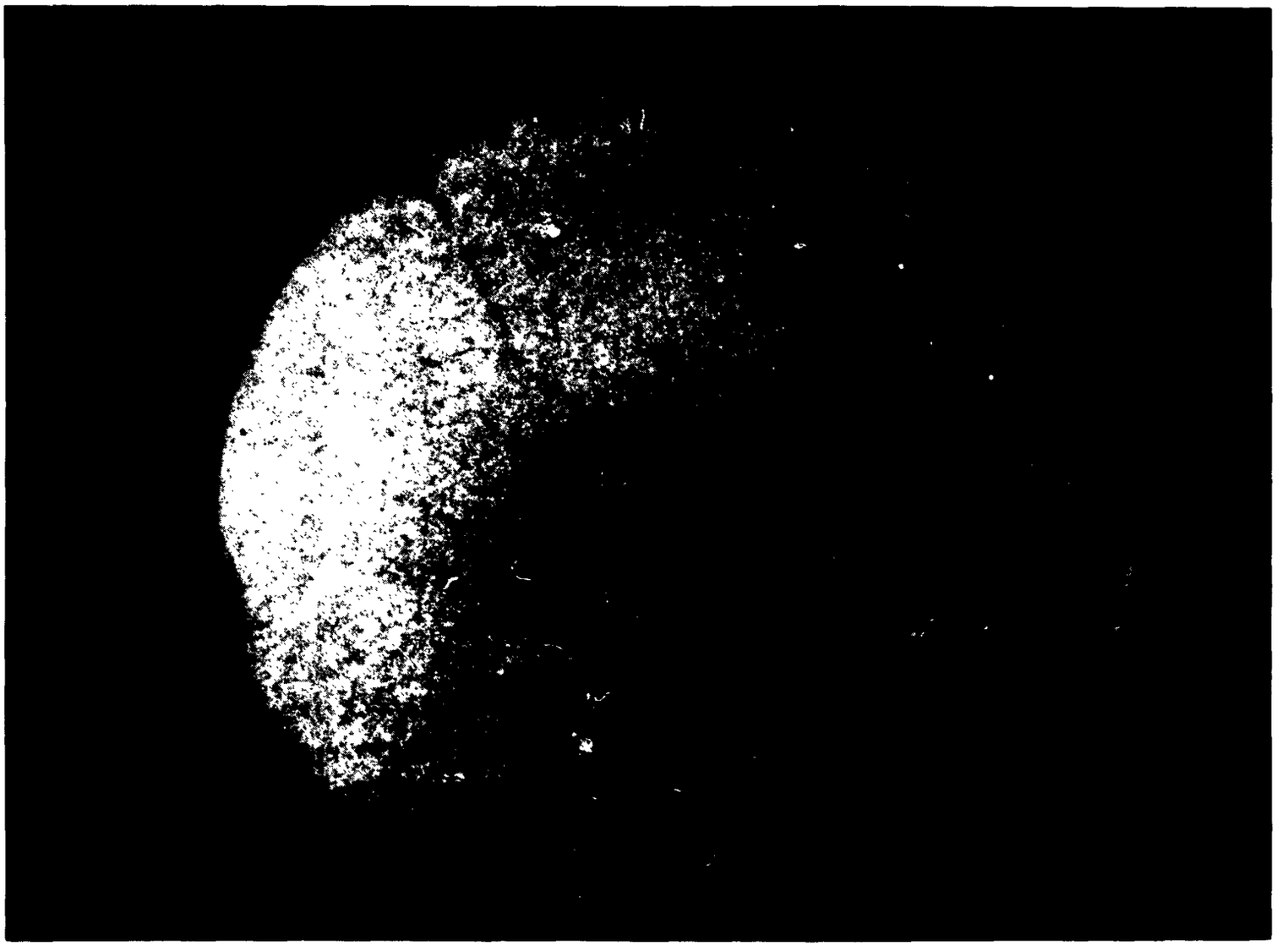


Figure 11. Uniform Work Function Area in Vapor Deposited Cathode – Emission Micrograph

V. OVERALL PROGRAM PROGRESS

This section briefly discusses and correlates the more significant achievements of the first year of the program, including the past (fourth) quarter.

At the beginning of the program several techniques, i.e., vapor disposition, skull casting, mechanical working, and chemical etching, were considered for producing uniform work functions. It was soon decided that chemical vapor deposition appeared most promising. Molybdenum was selected as the initial material for the study because of previous extensive experience in this laboratory with arc cast molybdenum.

The approach was an empirical one in which a search was made for preferred crystallographic orientation in vapor depositions produced by various processes and by variations of the individual process parameters. The substrate was arc cast molybdenum. Three basic processes were employed: pyrolysis of molybdenum pentachloride ($MoC\ell_5$), pyrolysis of molybdenum hexacarbonyl [$Mo(CO)_6$], and chemical reduction of molybdenum hexafluoride (MoF_6).

These three processes, in addition to involving different chemical reactions, covered a range of deposition temperatures from 200 to 1500°C. Variations in deposition rates and thicknesses were also studied. Stable adherent depositions were obtained with the chloride and fluoride processes. The carbonyl process was abandoned after several unsuccessful attempts to obtain satisfactory depositions.

X-ray techniques for determining the preferred orientation on curved surfaces were developed concurrently with the deposition program. Analysis of the vapor depositions showed the chloride pyrolysis and fluoride reduction processes to be each capable of producing both (111) and (100) fiber orientations. It was found, however, that stricter control of deposition conditions would be needed before reproducibility and uniformity of the preferred orientation over the entire surface could be obtained.

In addition to the x-ray analysis, all depositions were photomicrographed to determine grain structure. With the exception of the carbonyl deposits, all samples exhibited columnar grain growth.

Several cylindrical cathodes of the type used in thermionic converters were then produced using both the fluoride and the chloride processes. These were found to have (111) preferred orientations.

In conjunction with the above metallurgical program, it was necessary to develop techniques for observing the uniformity of work function of the vapor depositions and evaluating the effects in thermionic converters. Towards this end a thermionic emission electron microscope was constructed. The microscope is capable of resolving individual cathode grains and showing in high contrast the difference in emission between grains of different work function. The emission contrast is greater than previously obtained with the electron mirror microscope.

Several nonuniform vapor deposited and one arc cast molybdenum cathodes were observed in the microscope. Large variations in emission between adjacent grains were observed. Electropolishing was found to produce active patches. A vapor deposited cathode exhibiting areas of uniform work function was observed. It is believed that these grains corresponded to the low work function (111) planes. The dimensions of these uniform clusters were of the order of 1 mm on a side.

Another problem examined was the reproducibility of the characteristics of cylindrical cesium thermionic converters. Lack of reproducibility would make it difficult, if not impossible, to evaluate improvements in performance due to uniform work function cathodes. A cylindrical diode identical to diodes previously tested in the laboratory was constructed and its characteristics measured. It was found to reproduce optimized output data to within 5% at an emitter temperature of 1800°C, thus indicating that any subsequent improvements in performance obtained with vapor deposited cathodes will indeed be real effects.

Methods of surface preparation, a prime consideration in work function experiments, have been studied. The main difficulty anticipated was the fact that mechanical polishing creates a disturbed layer at the surface of the metal. At first, electropolishing was investigated as a solution to the problem and it was found that mirror finishes could be obtained with this technique. The effect of heat treatment in vacuum on a mechanically polished surface was also investigated. It was found that heating at 1800°C in vacuum was adequate to restore the surface to its original preferred orientation. This was due to a combination of evaporation of the Beilby layer and recrystallization of the deformed layer just beneath the surface.

VI. PROGRAM FOR THE NEXT QUARTER

Several changes are planned for the emission microscope in order to improve its resolution. They are:

a) Change to a shorter persistance phosphor to simplify focusing

b) Remove associated circuitry for higher voltages

c) Install a permanent camera support

d) Operate at higher voltages

e) Design a current measuring probe for obtaining quantitative measurements of emission differences.

The vapor deposition program will continue in order to achieve sample uniformity over larger areas. Emphasis will be on obtaining uniform gas flow conditions over the entire deposition area. It has been decided to change to tungsten for these continued studies. This decision is based on the following:

a) Tungsten is the most commonly used pure metal cathode material.

b) The parameters involved in tungsten deposition are easier to control than molybdenum. Experience has shown that useful depositions can be obtained over a wider range of parameters.

c) Visual observation indicates that deposition uniformity is obtained over larger areas for tungsten than for molybdenum.

d) Tungsten is the most thoroughly investigated metal with respect to thermionic properties. The work functions of its major crystallographic planes have been measured extensively, thus providing important data for comparison with the present program.

Changes in emission current density to be expected for uniform work function cathodes will be calculated.

REFERENCES

1. H. Johannson, Ann Physik 21, 274 (1934)
2. A. O. Jensen, "Research Program Related to Vapor Thermionic Converters for Nuclear Application, Quarterly Progress Report 27 September - 27 December 1962, Contract NAS3-2529," EOS Report 3410-Q-1
3. R. D. Heidenreich, J. App. Phys. 26, 757 (1955)
4. G. A. Haas, private communication

DISTRIBUTION

	Copies
ASD (ASRNET-3) (With Transmittal Letter) Wright-Patterson AFB, Ohio	2
ASD (ASRMFP-2) Wright-Patterson AFB, Ohio	1
AGED Attn: H. N. Serig 346 Broadway, 8th Floor New York 13, NY	4
ASTIA (TIPDR) Arlington Hall Stn Arlington 12, Va	10
Chief, BuShips Attn: Code 681A1D Navy Dept Wash 25, DC	1
Office of Naval Research Power Branch (Code 429) Attn: CDR J. J. Connelly Wash 25, DC	1
DRD (Army Reactor) USAEC (Bill Wendell) Mail Station F-311 Wash 25, DC	1
Commanding Officer USAEL (SELRA/PRT) Research Development Lab Attn: Dr. Dobischek Ft. Monmouth, NJ	1
USASRDL SIGRA/SL-PRT Ft. Monmouth, NJ	1
Ford Instrument Co Division of Sperry Rand Corp 31-10 Thomson Ave Long Island City 1, NY	1
General Atomic Attn: Dr. W. Pidd P. O. Box 608 San Diego 12, Calif	1
General Electric Microwave Lab Power Tube Dept Attn: Dr. Frank Palo Alto, Calif	1
General Electric Research Lab Attn: Dr. H. F. Webster Schenectady, NY	1
Allison Division General Motors Corp Attn: Mr. J. D. Dunlop Indianapolis, Ind	1
Hughes Research Labs Attn: Dr. Malcolm Currie 1313 Talbott Tower Dayton 2, Ohio	1
The Marquardt Corp Attn: Dr. R. A. Laubenstein 16555 Saticoy St Van Nuys, Calif	1
Microwave Electronics Attn: Dr. Robert W. DeGrasse 4061 Transport St Palo Alto, Calif	1
Radio Corporation of America David Sarnoff Research Center Attn: Dr. Paul Rappaport Princeton, NJ	1
Radio Corporation of America Electron Tube Division Attn: J. J. Polkosky Box 1140, New Holland Pike Lancaster, Pa	1
Raytheon Co General Research Labs Research Div, Spencer Lab Attn: Dr. P. A. Lindsay Burlington, Mass	1
Stanford Research Institute Physical Electronics Laboratory Attn: Mr. Donovan V. Geppert Menlo Park, Calif	1

DISTRIBUTION

	Copies
Thermo Electron Engr Corp Attn: E. N. Carabateas 85 First Ave Waltham 54, Mass	1
Varian Associates Attn: Dr. Daniel G. Dow 611 Hansen Way Palo Alto, Calif	1
Watkins-Johnson Co Stanford Industrial Park Attn: Dr. Dean Watkins Palo Alto, Calif	1
Westinghouse Electric Company Materials Engineering Attn: Dr. C. Goldberg Pittsburgh, Pa	1
Westinghouse Research Labs Attn: Dr. Milton Gottlieb Beulah Rd, Churchill Boro Pittsburgh 35, Pa	1